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The CD Spectra of Carbonato Complexes of the $[Co(CO_3)(O,O)(N)_2]^-$ and $[Co(CO_3)(N)_4]^+$ Types and Related Diaqua Complexes[1)]

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Five carbonato complexes, $[Co(CO_3)(ox)(tn)]^-$, *cis*-$[Co(CO_3)(ox)(py)_2]^-$, *cis*·*cis*-$[Co(CO_3)(NH_3)_2(py)_2]^+$, *cis*-$[Co(CO_3)(en)(py)_2]^+$, *cis*-$[Co(CO_3)(NH_3)_2(bpy)]^+$, and two related complexes, *cis*-$[Co(ox)(NH_3)_2(en)]^+$ and *cis*-$[Co(mal)(NH_3)_2(en)]^+$, have been prepared and resolved. The solution CD spectra of these resolved complexes and those of diaqua complexes derived from the carbonato complexes have been measured. The CD spectral comparison in the first absorption band (T_{1g}-band) region has suggested a relation in the sign of the Cotton peak between each of the carbonato complexes and the corresponding diaqua complex. Based on this relation, the assignments of the absolute configurations for the present complexes have been established.

It is known[2,3)] that the CD spectra of $(-)_{589}[Co(CO_3)(ox)(en)]^-$ and $(+)_{546}[Co(CO_3)(en)_2]^+$ exhibit a (+) Cotton peak in the first absorption band (T_{1g}-band) region, while the spectra for $(+)_{589}[Co(ox)(en)(H_2O)_2]^+$ and $(+)_{546}[Co(en)_2(H_2O)_2]^{3+}$, which are derived from the above carbonato complexes by acid-hydrolysis, show two peaks, (−) and (+), in the T_{1g}-band region. The absolute configurations of these carbonato complexes have been assigned to Λ based on a suggestion[2,3)] that the observed (+) peak is due to the $A_{1g}\rightarrow E_g$ (D_{4h}) transition component, while the absolute configurations of the corresponding diaqua complexes are also assigned to Λ based on the fact that acid-hydrolysis proceeds with retention of configuration. However, the (−) peak for $(+)_{589}[Co(ox)(en)(H_2O)_2]^+$ with CoN_2O_4 chromophore and the (+) peak for $(+)_{546}[Co(en)_2(H_2O)_2]^{3+}$ with CoN_4O_2 chromophore seem to be assignable to the $A_{1g}\rightarrow E_g$ transition component, when the ligand-field strengths of N and O are considered. In comparison of the CD signs due to the $A_{1g}\rightarrow E_g$ transition component, the sign of the $(-)_{589}$ carbonato complex is opposite to that of the $(+)_{589}$ diaqua complex, while the sign of the $(+)_{546}$ carbonato complex is the same as that of the $(+)_{546}$ diaqua complex. These different results come from the above-mentioned assignments of Cotton peaks, suggesting that the assignments are inconsistent.

In this work, the preparation and resolution of some new complexes of the $[Co(CO_3)(O,O)(N)_2]^-$ and $[Co(CO_3)(N)_4]^+$ types have been carried out. Optically active diaqua complexes have been also derived from the resolved carbonato complexes by acid-hydrolysis. In addition, this work has been extended to derive optically active oxalato complexes from the resolved carbonato complexes by a substitution reaction. The CD spectra of these active complexes have been measured and compared.

Experimental

Synthesis and Resolution. *a)* cis-*Diamminecarbonatoethylenediaminecobalt(III) Chloride Monohydrate,* cis-*$[Co(CO_3)(NH_3)_2(en)]Cl\cdot H_2O$*: This complex had been prepared by Bailar and Peppard,[4)] but we found another convenient method: to a solution of *cis*-$K[Co(CO_3)_2(en)]\cdot H_2O$ (35 g, 0.1 mol, in 150 cm^3 H_2O) were added concd aqueous ammonia (14 cm^3, 0.2 mol) and ammonium chloride (5.35 g, 0.1 mol); the mixture was then stirred at 50 °C until a red solution was obtained. The resulting solution, once filtered, was charged on a column containing Dowex 50W-X8 resin in Na^+ form (100—200 mesh, 7×8 cm). When the elution was carried out with a 0.15 M (1 M=1 mol/dm^3) NaCl aqueous solution, one red band descended. The effluent was concentrated to a small volume under reduced pressure; after being filtered once, the filtrate was kept in a refrigerator overnight. The deposited crystals were recrystallized from warm water. The yield was about 10 g. Found: C, 13.34; H, 6.12; N, 20.71%. Calcd for $[Co(CO_3)(NH_3)_2(C_2H_8N_2)]Cl\cdot H_2O$: C, 13.52; H, 6.00; N, 21.02%.

Though Hawkins *et al.* had resolved this complex using $[Co(SO_3)_2(NH_3)_2(R\text{-pn})]^-$ as the resolving agent,[5)] we resolved it with $(-)_{546}[Co(ox)_2(en)]^-$: the racemate (2 g, 0.008 mol) was dissolved in warm water (5 cm^3, *ca.* 35 °C), and $(-)_{546}Na[Co(ox)_2(en)]$ (1.3 g, 0.004 mol) was added to the solution. On cooling the whole solution in an ice-bath, a less soluble diastereoisomer containing the $(+)_{589}$ carbonato complex deposited. Recrystallization from water was repeated three times. The final yield was about 0.5 g. Found: C, 19.02; H, 4.86; N, 14.13%. Calcd for $[Co(CO_3)(NH_3)_2(C_2H_8N_2)][Co(C_2O_4)_2(C_2H_8N_2)]\cdot 2.5H_2O$: C, 18.92; H, 5.08; N, 14.72%.

b) cis-*Diammine(2,2′-bipyridine)carbonatocobalt(III) Chloride Dihydrate,* cis-*$[Co(CO_3)(NH_3)_2(bpy)]Cl\cdot 2H_2O$*: A solution of 2,2′-bipyridine (7.8 g, 0.05 mol) in 20 cm^3 CH_3OH was mixed with a solution of *cis*-$K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$ (12.5 g, 0.05 mol) in 20 cm^3 H_2O, and perchloric acid (30%) was then added dropwise to the mixture until the pH reached 5.5, with stirring in an ice-bath. After filtering off potassium perchlorate which precipitated, the filtrate was stirred at room temperature overnight. The resulting solution, filtered once, was poured into a column containing Dowex 50W-X8 in Na^+ form (100—200 mesh, 5×20 cm). Upon elution with a 0.2 M NaCl solution, only one red band descended. The eluate was concentrated to a small volume (*ca.* 20 cm^3). After removal of the sodium chloride by filtration, the filtrate was kept in a refrigerator to precipitate powdery crystals. The crystals were recrystallized from a minimum amount of warm water (*ca.* 30 °C). The yield was about 1.5 g. Found: C, 37.39; H, 4.08; N, 15.35%. Calcd for $[Co(CO_3)(NH_3)_2(C_{10}H_8N_2)]Cl\cdot 2H_2O$: C, 37.36; H, 4.24; N, 15.84%.

The $(+)_{546}Na[Co(edta)]$ complex (1.2 g, 0.0029 mol) was dissolved in a warm solution of the above racemate (2 g, 0.0058 mol, in 10 cm^3 H_2O). When the mixture was cooled in an ice-bath and the sides of the vessel were scratched with a glass rod, one diastereoisomeric salt of the $(+)_{589}$ carbonato complex precipitated. The recrystallization was repeated four times from water. The final yield was about

0.5 g. Found: C, 36.64; H, 4.16; N, 11.68%. Calcd for $[Co(CO_3)(NH_3)_2(C_{10}H_8N_2)][Co(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$: C, 36.41; H, 4.33; N, 12.14%.

c) cis·cis-Diamminecarbonatobis(pyridine)cobalt(III) Chloride Monohydrate, cis·cis-$[Co(CO_3)(NH_3)_2(py)_2]Cl\cdot 2H_2O$: An appropriate amount of 60% $HClO_4$ was added dropwise to a mixture of $K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$ (10 g, 0.036 mol, in 20 cm^3 H_2O) and pyridine (6 cm^3, 0.072 mol) in an ice-bath in order to adjust the pH to 5.5. After filtration, the filtrate was stirred at room temperature for some time. Some pink crystals deposited. A solution of the crude product was poured into a column of Dowex 50W-X8 resin in Na^+ form. The effluent obtained by elution with a 0.3 M NaCl was concentrated to a small volume (*ca.* 10 cm^3). When the solution was kept in a refrigerator, red crystals deposited. These were recrystallized from warm water (*ca.* 35 °C). The yield was about 1.0 g. Found: C, 36.07; H, 4.93; N, 15.55%. Calcd for $[Co(CO_3)(C_5H_5N)_2(NH_3)_2]Cl\cdot H_2O$: C, 36.23; H, 4.98; N, 15.36%.

Into a solution of this racemate (3.3 g, 0.009 mol, in 10 cm^3 H_2O) was poured a resolving agent, $(-)_{546}Na[Co(ox)_2(en)]\cdot H_2O$ (1.2 g, 0.0038 mol), with stirring. The less soluble diastereoisomer containing the $(-)_{589}$-isomer of the carbonato complex crystallized out when the solution was allowed to stand in an ice-bath. This was recrystallized from water. The final yield was about 0.3 g. Found: C, 31.37; H, 4.67; N, 12.82%. Calcd for $[Co(CO_3)(NH_3)_2(C_5H_5N)_2][Co(C_2O_4)_2(C_2H_8N_2)]\cdot 2.5H_2O$: C, 31.35; H, 4.49; N, 12.90%.

d) cis-Carbonatoethylenediaminebis(pyridine)cobalt(III) Chloride Monohydrate, cis-$[Co(CO_3)(py)_2(en)]Cl\cdot H_2O$: This complex was prepared in the same way as described in c) except for the use of $K[Co(CO_3)_2(en)]\cdot H_2O$ (10 g, 0.034 mol, in 20 cm^3 H_2O). The reacted solution, filtered once, was chromatographed on a column of Dowex 50W-X8 resin in Na^+ form (100—200 mesh, 5×25 cm) using 0.1 M NaCl as the eluting solution. Two bands colored pink and red descended. The eluate of the red band was collected in a fraction, and concentrated to a small volume (*ca.* 10 cm^3). After filtration, the filtrate was kept in a refrigerator (*ca.* 4 h). The crude precipitates thus obtained were recrystallized from warm water. The yield was about 2 g. Found: C, 39.72; H, 5.02; N, 14.01%. Calcd for $[Co(CO_3)(C_2H_8N_2)(C_5H_5N)_2]Cl\cdot H_2O$: C, 39.95; H, 5.12; N, 14.24%.

$(-)_{546}Na[Co(ox)_2(en)]\cdot H_2O$ (1.6 g, 0.005 mol) was dissolved in a hot solution of the racemate (3.9 g, 0.01 mol, in 10 cm^3 H_2O), followed by addition of ethanol (*ca.* 2 cm^3). The mixture was cooled in an ice-bath and the sides of the vessel were scratched with a glass rod, whereupon the diastereoisomeric salt of the $(-)_{589}$ carbonato complex deposited. The salt was collected and recrystallized four times from warm water (*ca.* 35 °C). The final yield was about 0.7 g. Found: C, 34.24; H, 4.40; N, 12.52%. Calcd for $[Co(CO_3)(C_2H_8N_2)(C_5H_5N)_2][Co(C_2O_4)_2(C_2H_8N_2)]\cdot 2H_2O$: C, 34.16; H, 4.52; N, 12.57%.

e) Sodium Carbonatooxalatotrimethylenediaminecobaltate(III), $Na[Co(CO_3)(ox)(tn)]$: Trimethylenediamine (7.4 g, 0.1 mol) and oxalic acid (12.6 g, 0.1 mol) were mixed with stirring in an ice-bath, and then ethanol was added until trimethylenediammonium oxalate deposited. This product (6.7 g, 0.05 mol) was added to a green solution of $[Co(CO_3)_3]^{3-}$ ($Co(NO_3)_2\cdot 6H_2O$ 15 g, 0.05 mol scale). The mixture was stirred at 45 °C until the color of the solution became blue-violet, and then the resulting solution was concentrated to a small volume under reduced pressure. After filtration, the filtrate was chromatographed using a column containing Dowex 1X-8 resin in Cl^- form (5×20 cm) and 0.1 M NaCl as the eluent; one blue-violet band came out. The eluate was concentrated to a small volume under reduced pressure, and after being filtered once, was kept in a refrigerator (*ca.* 1 h). The crude product thus obtained was recrystallized from warm water. The yield was about 3 g. Found: C, 23.52; H, 3.20; N, 9.03%. Calcd for $Na[Co(CO_3)(C_2O_4)(C_3H_{10}N_2)]$: C, 23.68; H, 3.29; N, 9.21%.

A mixture of the racemate (2 g, 0.006 mol) and $(-)_{589}$-$[Co(ox)(en)_2](C_2H_3O_2)$ (0.9 g, 0.003 mol) in water (10 cm^3) was cooled in an ice-bath. Immediately a less soluble diastereoisomeric salt of the $(-)_{589}$ carbonato complex deposited. The recrystallization was repeated five times from water. The final yield was about 0.4 g. Found: C, 24.10; H, 5.09; N, 13.40%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2][Co(CO_3)(C_2O_4)(C_3H_{10}N_2)]\cdot 3H_2O$: C, 23.93; H, 5.32; N, 13.95%.

f) cis-Bis(ethylenediamine)dinitrocobalt(III) cis-Carbonatooxalatobis(pyridine)cobaltate(III) Dihydrate, cis-$[Co(NO_2)_2(en)_2]$*-cis-*$[Co(CO_3)(ox)(py)_2]\cdot 2H_2O$: To a concentrated solution of *cis*-$[Co(CO_3)(ox)(py)_2]^-$, which was prepared by the literature method[6] ($Co(NO_3)_2\cdot 6H_2O$, 15 g scale, 0.05 mol), was added *cis*-$[Co(NO_2)_2(en)_2](C_2H_3O_2)$ (8.25 g, 0.025 mol). The mixture was kept in a refrigerator until a less soluble salt deposited; this was then recrystallized from warm water. Found: C, 30.33; H, 4.34; N, 16.24%. Calcd for $[Co(NO_2)_2(C_2H_8N_2)_2][Co(CO_3)(C_2O_4)(C_5H_5N)_2]\cdot 2H_2O$: C, 30.36; H, 4.46; N, 16.67%.

The resolving agent $(-)_{589}[Co(NO_2)_2(en)_2]I$ (1 g, 0.0025 mol) was converted into the acetate with silver acetate (0.4 g, 0.0025 mol). The compound, $[Co(NO_2)_2(en)_2][Co(CO_3)(ox)(py)_2]\cdot 2H_2O$ (3 g, 0.005 mol), was dissolved in water (30 cm^3) and converted into sodium salt by passing the solution through a column of Dowex 50W-X8 resin in Na^+ form. After the column had been rinsed thoroughly with water, the whole effluent was concentrated to a small volume (*ca.* 10 cm^3). The concentrate was added to the solution of the above resolving agent. When the mixed solution was kept in a refrigerator, the precipitates obtained soon were optically inactive, and subsequently the desired diastereoisomer containing the $(+)_{589}$ carbonato complex was obtained. The yield was about 0.05 g. Found: C, 30.33; H, 4.34; N, 16.24%. Calcd for $[Co(NO_2)_2(C_2H_8N_2)_2][Co(CO_3)(C_2O_4)(C_5H_5N)_2]\cdot 2H_2O$: C, 30.36; H, 4.46; N, 16.67%.

g) cis-Diammineethylenediamineoxalatocobalt(III) Chloride Monohydrate, cis-$[Co(ox)(NH_3)_2(en)]Cl\cdot H_2O$: The preparation of this complex from trans(NH$_3$)-$[Co(Cl)_2(NH_3)_2(en)]Cl$ has been reported.[4] In our work, *cis*-$[Co(CO_3)(NH_3)_2(en)]Cl\cdot H_2O$ was used as the starting material. To a mixture of *cis*-$[Co(CO_3)(NH_3)_2(en)]Cl\cdot H_2O$ (10 g, 0.04 mol) and $K_2C_2O_4\cdot H_2O$ (7 g, 0.04 mol) in water (20 cm^3), was added a solution of $H_2C_2O_4\cdot 2H_2O$ (5 g, 0.04 mol, in 10 cm^3 H_2O) dropwise in an ice-bath. The solution was further stirred at 40 °C for 3 h. After filtering the solution, the filtrate was charged on a column containing Dowex 50W-X8 resin Na^+ form (4×20 cm). By elution with a 0.1 M NaCl solution, one band descended. The effluent was concentrated to a small volume, and this concentrated solution was filtered and then kept in a refrigerator. The red crystals which deposited were recrystallized from warm water (*ca.* 35 °C). The yield was about 7 g. Found: C, 16.26; H, 5.48; N, 19.15%. Calcd for $[Co(C_2O_4)(NH_3)_2(C_2H_8N_2)]Cl\cdot H_2O$: C, 16.30; H, 5.43; N, 19.02%.

The $[Co(ox)(NH_3)_2(en)]Cl\cdot H_2O$ complex (2 g, 0.007 mol) was converted to the acetate with silver acetate (1.2 g, 0.007 mol). On adding $(-)_{546}Na[Co(ox)_2(en)]\cdot H_2O$ (1.12 g, 0.0035 mol) to a solution of the acetate in 20 cm^3 water, a less soluble diastereoisomer containing the $(+)_{589}$ isomer of the cation separated out. The salt was recrystallized five times from warm water (*ca.* 35 °C). The final yield was about 0.4 g. Found: C, 21.49; H, 4.39; N, 14.86%. Calcd for $[Co(C_2O_4)(NH_3)_2(C_2H_8N_2)][Co(C_2O_4)_2(C_2H_8N_2)]\cdot H_2O$: C, 21.66; H, 4.34; N, 15.16%.

h) cis-*Diammineethylenediaminemalonatocobalt(III) Chloride 0.5-Hydrate,* cis-$[Co(mal)(NH_3)_2(en)]Cl\cdot 0.5H_2O$: An aqueous solution of *cis*-$[Co(CO_3)(NH_3)_2(en)]Cl\cdot H_2O$ (10 g, 0.004 mol, in 20 cm^3 H_2O) was treated in the same way as described in g) except for the use of potassium malonate (7 g, 0.04 mol) and malonic acid (4 g, 0.04 mol). The yield was about 4 g. Found: C, 20.16; H, 5.75; N, 19.07%. Calcd for $[Co(C_3H_2O_4)(NH_3)_2(C_2H_8N_2)]Cl\cdot 0.5H_2O$: C, 20.04; H, 5.67; N, 18.70%.

This complex was resolved by column chromatography: a solution of the racemic chloride complex was charged on a column containing Dowex 50W-X8 resin in Na$^+$ form (2×40 cm). Elution with a 0.1 M $K_2[Sb_2(d\text{-tart})_2]$ aqueous solution resulted in a partial resolution. The specific rotation of the later effluent was positive at 589 nm.

Derivation from Optically Active Complex *a)* $(+)_{546}[Co(ox)(en)_2]^+$: The compound, $(+)_{546}[Co(CO_3)(en)_2](+)_{546}[Co(ox)_2(en)]$ was dissolved in water and converted into the chloride by passing the solution through a column (5×2 cm) of Dowex 1-X8 resin in Cl$^-$ form. After being washed with water, the whole effluent was concentrated to a small volume. To the concentrated solution was added a solution of $H_2C_2O_4\cdot 2H_2O$ dropwise in an ice-bath, and then the solution was stirred at 40 °C for 3 h. The resulting solution was charged on a column of Dowex 50W-X8 resin in Na$^+$ form. The elution was carried out with a 0.1 M NaCl solution, whereby one band descended. The absorption and CD spectral data of this effluent were identical with those of $(+)_{546}[Co(ox)(en)_2]^+$.[3]

b) $(+)_{589}[Co(ox)(NH_3)_2(en)]^+$: This complex was prepared in the same way as described in a) except for the use of $(+)_{589}[Co(CO_3)(NH_3)_2(en)]^+$ instead of $(+)_{546}[Co(CO_3)(en)_2]Cl$. The effluent showed the same absorption and CD spectra as those of $(+)_{589}[Co(ox)(NH_3)_2(en)]^+$.

c) $(-)_{546}[Co(ox)_2(en)]^-$: A solution of $H_2C_2O_4\cdot 2H_2O$ was added to a solution of $(-)_{589}[Co(CO_3)(ox)(en)]^-$ little by little with stirring in an ice-bath. After the resulting solution was stirred at 50 °C for a while, the solution was chromatographed on a column of Dowex 1-X8 resin in Cl$^-$ form using a 0.1 M NaCl solution. Only one band descended. The absorption and CD spectra of this effluent was identical to those of $(-)_{546}[Co(ox)_2(en)]^-$.

Measurement. The absorption spectra in aqueous solution were recorded with a Hitachi 323 recording spectrophotometer. In the case of the *cis*-$[Co(CO_3)(ox)(py)_2]^-$ complex, the spectrum was measured with a solution passed through a cation exchange resin in Na$^+$ form in order to remove the counter ion, $[Co(NO_2)_2(en)_2]^+$. For the CD spectral measurements, a JASCO J-40CS automatic recording spectropolarimeter with a JASCO Model J-DPZ data processor was used; a JASCO Model DIP-SL automatic polarimeter was used for optical rotation measurements. In both cases, samples were converted into the same cations and anions as those of the corresponding racemates by means of ion-exchange techniques.

The absorption and CD spectra of the diaqua complex species were measured with solutions of the carbonato complexes acidified with 10% $HClO_4$. The absorption and CD spectra of the acidified solutions were reformed into the spectra of the parent carbonato complexes when potassium hydrogencarbonate was added to the acidified solutions. This result suggests that the acid hydrolyses proceed with retention of the configurations.

Results and Discussion

CD Spectra. The absorption spectra of the new complexes are shown in Figs. 1 and 2. The CD spectra for the complexes of the types $[Co(O,O)_2(N)_2]^-$, $[Co(O,O)(N)_4]^+$, $[Co(O,O)(N)_2(H_2O)_2]^+$, and $[Co(N)_4(H_2O)_2]^{3+}$ (O,O=CO_3^{2-}, ox^{2-}, and mal^{2-}; $(N)_2$=2NH$_3$, 2py, en, tn, and bpy) are shown in Figs. 3—7, while the numerical data are summarized in Tables 1 and 2. We are interested in the comparison of the CD spectra in the T_{1g}-band region; hereafter, only the spectra observed in the region are discussed.

The CD spectra of $(+)_{546}[Co(CO_3)(en)_2]^+$, $(+)_{589}$-

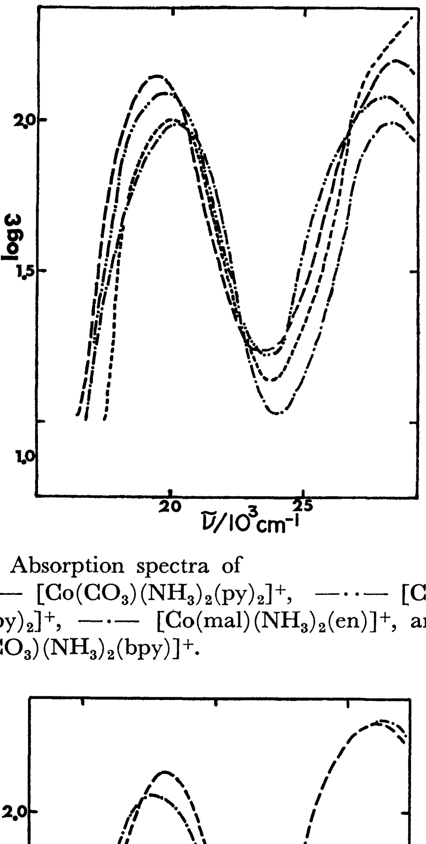

Fig. 1. Absorption spectra of ——— $[Co(CO_3)(NH_3)_2(py)_2]^+$, —··— $[Co(CO_3)(en)(py)_2]^+$, —·— $[Co(mal)(NH_3)_2(en)]^+$, and ---- $[Co(CO_3)(NH_3)_2(bpy)]^+$.

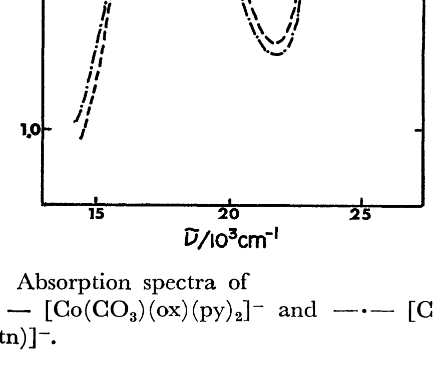

Fig. 2. Absorption spectra of ——— $[Co(CO_3)(ox)(py)_2]^-$ and —·— $[Co(CO_3)(ox)(tn)]^-$.

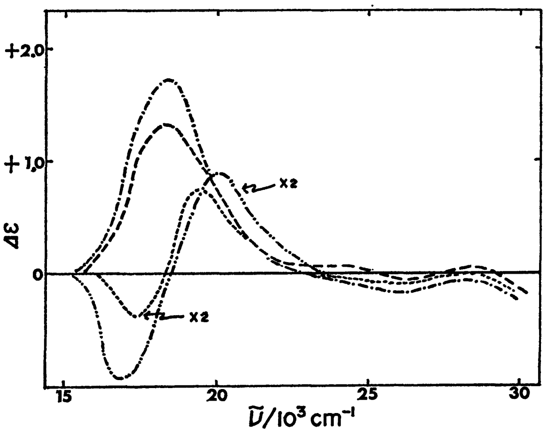

Fig. 3. CD spectra of — — — $(+)_{589}[\mathrm{Co(CO_3)(ox)(tn)}]^-$, —··— $(+)_{589}[\mathrm{Co(ox)(tn)(H_2O)_2}]^+$, —·— $(+)_{589}[\mathrm{Co(CO_3)(ox)(py)_2}]^-$, and ---- $(+)_{589}[\mathrm{Co(ox)(py)_2(H_2O)_2}]^+$.

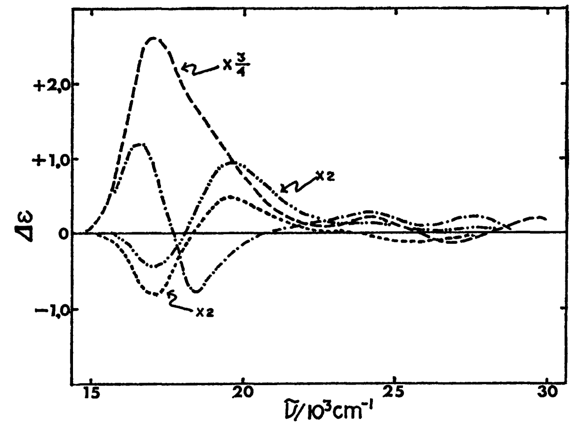

Fig. 4. CD spectra of — — — $(-)_{589}[\mathrm{Co(CO_3)(ox)(en)}]^-$, —··— $(+)_{589}[\mathrm{Co(ox)(en)(H_2O)_2}]^+$, —·— $(-)_{589}[\mathrm{Co(CO_3)(mal)(NH_3)_2}]^-$, and ---- $(+)_{589}[\mathrm{Co(mal)(NH_3)_2(H_2O)_2}]^+$.

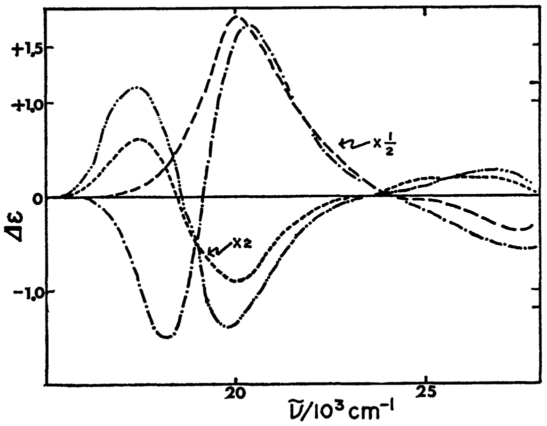

Fig. 5. CD spectra of —·— $(-)_{589}[\mathrm{Co(CO_3)(NH_3)_2(py)_2}]^+$, ----$(-)_{589}[\mathrm{Co(NH_3)_2(py)_2(H_2O)_2}]^{3+}$, — — — $(+)_{589}[\mathrm{Co(CO_3)(en)(py)_2}]^+$, and —··— $(-)_{589}[\mathrm{Co(en)(py)_2(H_2O)_2}]^{3+}$.

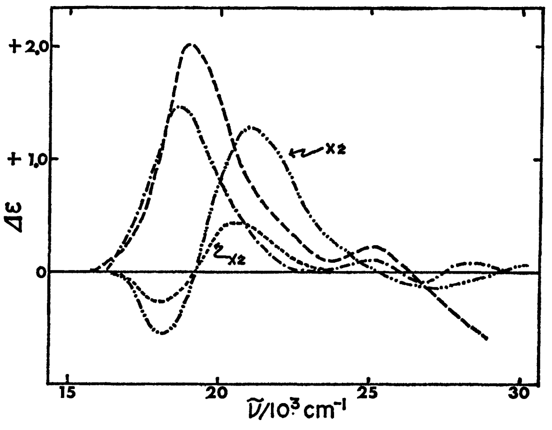

Fig. 6. CD spectra of — — — $(+)_{589}[\mathrm{Co(CO_3)(NH_3)_2(bpy)}]^+$, —··— $(+)_{589}[\mathrm{Co(NH_3)_2(bpy)(H_2O)_2}]^{3+}$, —·— $(+)_{589}[\mathrm{Co(CO_3)(NH_3)_2(en)}]^+$, and ---- $(-)_{589}[\mathrm{Co(NH_3)_2(en)(H_2O)_2}]^{3+}$.

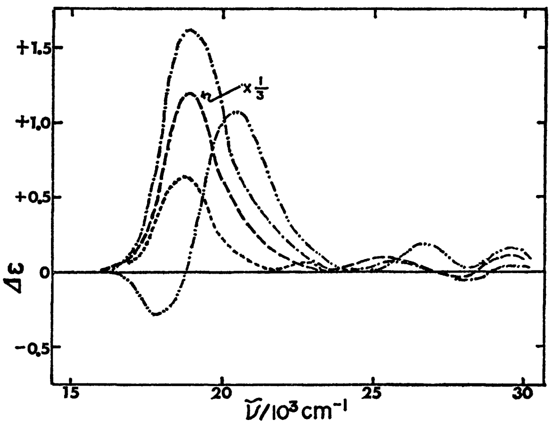

Fig. 7. CD spectra of — — — $(+)_{546}[\mathrm{Co(CO_3)(en)_2}]^+$, —··— $(+)_{546}[\mathrm{Co(en)_2(H_2O)_2}]^{3+}$, —·— $(+)_{589}[\mathrm{Co(ox)(NH_3)_2(en)}]^+$, and ---- $(+)_{589}[\mathrm{Co(mal)(NH_3)_2(en)}]^+$.

$[\mathrm{Co(CO_3)(NH_3)_2(en)}]^+$ and $(+)_{589}[\mathrm{Co(CO_3)(NH_3)_2(bpy)}]^+$ show one (+) peak. On the other hand, the CD spectra of the diaqua complexes derived from the above carbonato complexes show (−) and (+) peaks from the lower frequncy side. The CD spectrum of $(-)_{589}[\mathrm{Co(CO_3)(NH_3)_2(py)_2}]^+$ shows (−) and (+) peaks from the lower frequency side and the (+) peak is dominant. The CD spectrum of $(+)_{589}[\mathrm{Co(CO_3)(en)(py)_2}]^+$ shows one (+) peak. The CD spectra of the diaqua complexes, $(-)_{589}[\mathrm{Co(NH_3)_2(py)_2(H_2O)_2}]^{3+}$ and $(-)_{589}[\mathrm{Co(en)(py)_2(H_2O)_2}]^{3+}$, derived from the above bis(pyridine) complexes by the acid hydrolyses show (+) and (−) peaks from the lower frequency side. The CD spectra of the carbonato complexes suggest that the above five carbonato complexes have the same absolute configuration. On the other hand, the CD spectra of the diaqua complexes suggest that the absolute configurations of the first three carbonato complexes are opposite to those of the last two carbonato complexes, since the acid hydrolyses proceed with retention of the configurations. Thus, the relative configurations based on the CD spectra of the carbonato complexes don't agree with those based on the CD spectra of the corresponding diaqua complexes in the bis(pyridine) complexes.

The CD spectra of $(-)_{589}[\mathrm{Co(CO_3)(ox)(en)}]^+$,

Table 1. Spectral data

Complex	Absorption	CD
	$\tilde{\nu}_{\mathrm{max}}$[a] $(\log \varepsilon)$	$\tilde{\nu}_{\mathrm{max}}$[a] $(\Delta\varepsilon)$
$(-)_{589}[\mathrm{Co(CO_3)(ox)(en)}]^-$ [b]	18.1(2.16)	17.2(+3.43)
	25.6(2.25)	23.9(+0.33)
		25.9(−0.07)
		28.3(+0.21)
$(+)_{589}[\mathrm{Co(ox)(en)(H_2O)_2}]^+$ [b]	18.1(1.94)	17.3(−0.47)
		19.7(+0.99)
	26.2(2.06)	23.8(+0.16)
		27.9(+0.18)
$(+)_{589}[\mathrm{Co(CO_3)(ox)(tn)}]^-$	17.8(2.08)	18.3(+1.27)
	25.8(2.29)	23.8(+0.09)
		25.8(−0.06)
$(+)_{589}[\mathrm{Co(ox)(tn)(H_2O)_2}]^+$	18.2(1.84)	16.8(−0.43)
		19.3(+0.52)
	26.2(2.14)	26.0(−0.01)
		31.3(−0.02)
$(+)_{589}[\mathrm{Co(CO_3)(ox)(py)_2}]^-$	18.0(2.14)	18.4(+0.87)
	25.6(2.28)	25.9(−0.10)
$(+)_{589}[\mathrm{Co(ox)(py)_2(H_2O)_2}]^+$	18.3(1.91)	17.5(−0.19)
		19.4(+0.40)
	25.5(2.14)	26.0(−0.10)
$(-)_{589}[\mathrm{Co(CO_3)(mal)(NH_3)_2}]^-$ [b]	17.8(2.00)	16.5(+1.21)
		18.4(−0.81)
	25.7(2.14)	23.9(+0.28)
		27.2(+0.26)
$(+)_{589}[\mathrm{Co(mal)(NH_3)_2(H_2O)_2}]^+$ [b]	18.3(1.72)	17.0(−0.42)
		19.4(+0.49)
	26.4(1.89)	26.1(−0.04)
$(+)_{589}[\mathrm{Co(CO_3)(ox)(NH_3)_2}]^-$ [c]	17.7(2.09)	17.3(+1.74)
	25.7(2.18)	23.6(+0.22)
		25.8(−0.11)
		28.3(+0.09)
$(+)_{589}[\mathrm{Co(ox)(NH_3)_2(H_2O)_2}]^+$ [c]	18.2(1.84)	16.60(−0.76)
		19.37(+0.58)
	26.2(2.02)	

a) ν_{max} values in $10^3\ \mathrm{cm}^{-1}$. b) Spectral data are in Ref. 2. c) Spectral data are in Ref. 10.

Table 2. Spectral data

Complex	Absorption	CD
	$\tilde{\nu}_{\mathrm{max}}$[a] $(\log \varepsilon)$	$\tilde{\nu}_{\mathrm{max}}$[a] $(\Delta\varepsilon)$
$(+)_{589}[\mathrm{Co(CO_3)(NH_3)_2(en)}]^+$	19.4(2.08)	18.8(+1.53)
	27.9(2.08)	25.5(+1.30)
		27.4(−0.05)
		30.1(+0.11)
$(+)_{589}[\mathrm{Co(NH_3)_2(en)(H_2O)_2}]^{3+}$	20.1(1.97)	18.1(−0.17)
		20.6(+0.22)
	27.9(1.96)	25.3(+0.01)
$(+)_{546}[\mathrm{Co(CO_3)(en)_2}]^+$ [b]	19.4(2.16)	18.7(+3.70)
	27.7(2.12)	25.6(+0.27)
		27.5(−0.10)
		29.1(+0.15)
$(+)_{546}[\mathrm{Co(en)_2(H_2O)_2}]^{3+}$ [b]	20.2(1.92)	17.9(−0.3)
		20.6(+1.05)
	27.7(1.82)	26.5(+0.20)
		29.4(+0.15)
$(+)_{589}[\mathrm{Co(CO_3)(NH_3)_2(bpy)}]^+$	19.5(2.07)	19.0(+2.03)
		25.3(+0.25)
		29.2(−0.66)
$(+)_{589}[\mathrm{Co(NH_3)_2(bpy)_2(H_2O)_2}]^{3+}$	20.1(1.82)	18.2(−0.29)
		21.1(+0.66)
		26.5(−0.05)
		28.8(+0.11)
$(-)_{589}[\mathrm{Co(CO_3)(NH_3)_2(py)_2}]^+$	19.4(2.06)	18.1(−0.59)
		20.3(+0.92)
	27.6(2.07)	27.8(−0.28)
$(-)_{589}[\mathrm{Co(NH_3)_2(py)_2(H_2O)_2}]^{3+}$	19.7(1.83)	17.4(+0.15)
		19.8(−0.22)
	28.3(1.83)	26.5(+0.05)
$(+)_{589}[\mathrm{Co(CO_3)(en)(py)_2}]^+$	19.5(2.09)	20.0(+1.87)
	27.6(2.09)	27.4(−0.36)
$(-)_{589}[\mathrm{Co(en)(py)_2(H_2O)_2}]^{3+}$	20.1(1.92)	17.4(+0.59)
		19.8(−0.72)
	27.8(1.92)	25.7(+0.08)
$(+)_{589}[\mathrm{Co(ox)(NH_3)_2(en)}]^+$	19.8(2.03)	19.1(+1.65)
	28.1(2.17)	25.5(+0.13)
		27.5(−0.04)
		29.7(+0.06)
$(+)_{589}[\mathrm{Co(mal)(NH_3)_2(en)}]^+$	19.9(1.99)	18.3(+0.66)
		22.2(+0.07)
	28.1(1.99)	25.6(+0.03)
		27.2(−0.02)
		29.5(+0.14)

a) $\tilde{\nu}_{\mathrm{max}}$ values in $10^3\ \mathrm{cm}^{-1}$. b) Spectral data are in Ref. 3.

$(+)_{589}[\mathrm{Co(CO_3)(ox)(NH_3)_2}]^-$,[2] $(+)_{589}[\mathrm{Co(CO_3)(ox)(tn)}]^-$ and $(+)_{589}[\mathrm{Co(CO_3)(ox)(py)_2}]^-$ have all one (+) peak, and those of the diaqua complexes derived from the above carbonato complexes have (−) and (+) peaks from the lower frequency side. The CD spectrum of $(-)_{589}[\mathrm{Co(CO_3)(mal)(NH_3)_2}]^-$ [2] shows (+) and (−) peaks, in which the (+) peak at the lower frequency side is dominant. The CD spectrum of $(-)_{589}[\mathrm{Co(mal)(NH_3)_2(H_2O)_2}]^+$ derived from the above malonato complex shows (−) and (+) peaks from the lower frequency side. The CD spectra of these carbonato complexes suggest that the above five carbonato complexes have the same absolute configuration. The CD spectra of the corresponding diaqua complexes also suggest that the above five carbonato complexes have the same absolute configuration.

Assignment of Transition Component. In order to understand the various CD patterns in the T_{1g}-band region for a series of the $[\mathrm{Co(O,O)_2(N)}]^-$-type complexes, Muramoto *et al.* attempted to analyze the observed patterns into Gaussian curves.[2] In this analysis, the CD curve was resolved into two components of opposite sign. The results showed that every pattern was a curve which resulted from the mutual cancellation of a component at a lower frequency and a component at a higher frequency, and that the component at the lower frequency never changed its CD sign due to the mutual cancellation. With the $[\mathrm{Co(O,O)_2(N)_2}]^-$-type complexes, since the $A_{1g} \rightarrow A_{2g}$ (D_{4h}) transition lies at a higher frequency than the $A_{1g} \rightarrow E_g$ transition, the CD peak at the lower frequency is assigned to the component corresponding to the latter transition (*i.e.* E_g component). From this assignment, the dominant peak in the spectrum of a $[Co(CO_3)(O,O)(N)_2]^-$-type complex is assignable to the E_g component. Since the CD spectrum of a $[Co(O,O)(N)_2(H_2O)_2]^+$-type complex shows two Cotton peaks with opposite sign, the peak at a lower frequency is assignable to the E_g component. From these assignments, the Cotton peak of the $A_{1g}\rightarrow E_g$ transition component for a $[Co(CO_3)(O,O)(N)_2]^-$-type complex has the opposite sign to that for the corresponding diaqua complex.

The CD spectrum of $(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$ and that of $(-)_{589}[Co(NH_3)_2(py)_2(H_2O)_2]^{3+}$ show (−) and (+) peaks and (+) and (−) peaks, respectively. Since the $A_{1g}\rightarrow E_g$ transition lies at a higher frequency than the $A_{1g}\rightarrow A_{2g}$ one in the case of the $[Co(O)_2(N)_4]^+$-type complexes, the (−) peak of the former complex and the (+) peak of the latter complex are both assignable to the $A_{1g}\rightarrow A_{2g}$ transition component (*i.e.* A_{2g} component).

The CD spectra of $(+)_{589}[Co(mal)(NH_3)_2(en)]^+$ and $(+)_{589}[Co(mal)(en)_2]^+$ [7] show two peaks of the same sign. On the other hand, the CD spectrum of $(-)_{589}[Co(ox)_2(NH_3)_2]^-$ [2] shows also (+) and (+) peaks and the dominant peak lies at the lower frequency side in the T_{1g}-band region. In the Gaussian analysis, the CD spectrum of $(-)_{589}[Co(ox)_2(NH_3)_2]^-$ was resolved into a (+) component at a lower frequency and a (−) component at a higher frequency. Since the major peaks for the above malonato complexes with CoN_4O_2 chromophore lie at a lower frequency than the minor peaks, if the observed CD spectra are resultant curves from the mutual cancellation of two components, which have opposite signs and correspond to the $A_{1g}\rightarrow A_{2g}$ and $A_{1g}\rightarrow E_g$ transitions, the two CD peaks of both malonato complexes are residues of the peak corresponding to the A_{2g} component.

A comparison of the CD spectra of $(+)_{546}[Co(CO_3)(en)_2]^+$, $(+)_{546}[Co(ox)(en)_2]^+$,[7] and $(+)_{589}[Co(mal)(en)_2]^+$ shows that the intensities of their dominant Cotton peaks decrease in the order of the carbonato, oxalato, and malonato complexes. Since the (+) Cotton peak of $(+)_{589}[Co(mal)(en)_2]^+$ has been assigned to the A_{2g} component, this change can be explained by considering that the intensity of the E_g component, which has a negative sign, increases according to the change in the O,O ligands. Therefore, the dominant CD peak of $(+)_{546}[Co(CO_3)(en)_2]^+$ is also assigned to the A_{2g} component.

Since the CD spectra of $(+)_{589}[Co(CO_3)(NH_3)_2(en)]^+$, $(+)_{589}[Co(ox)(NH_3)_2(en)]^+$ and $(+)_{589}[Co(mal)(NH_3)_2(en)]^+$ have the same CD patterns as those of $(+)_{546}[Co(CO_3)(en)_2]^+$, $(+)_{546}[Co(ox)(en)_2]^+$ and $(+)_{589}[Co(mal)(en)_2]^+$, respectively, the dominant peaks of these diammine-type complexes can be assigned to the A_{2g} component. On the other hand, since the CD spectra of $(+)_{546}[Co(en)_2(H_2O)_2]^{3+}$ and $(+)_{589}[Co(NH_3)_2(en)(H_2O)_2]^{3+}$ show (−) and (+) peaks from the lower frequency side, the Cotton peak at the lower frequency side in the T_{1g}-band region for $(+)_{546}[Co(en)_2(H_2O)_2]^{3+}$ or $(+)_{589}[Co(NH_3)_2(en)(H_2O)_2]^{3+}$ is also assignable to the A_{2g} component.

From these discussions, it may be concluded that the dominant Cotton peaks for the $[Co(O,O)(N)_4]^+$-type complexes are not always assignable to the E_g component and that the sign of the Cotton peak corresponding to the $A_{1g}\rightarrow A_{2g}$ for a complex of the $[Co(CO_3)(N)_4]^+$-type is opposite to that for the $[Co(N)_4(H_2O)_2]^{3+}$ complex derived from the acid-hydrolysis of the carbonato complex.

Since the CD spectrum of $(+)_{589}[Co(CO_3)(en)(py)_2]^+$ shows one (+) peak in the T_{1g}-band region and that of the corresponding diaqua complex shows (+) and (−) peaks from the lower frequency side, the (+) peak for $(+)_{589}$ carbonato complex can be assigned to the E_g component from the above conclusion. On the other hand, since the CD spectrum of $(+)_{589}[Co(CO_3)(NH_3)_2(bpy)]^+$ shows one (+) peak and that of the corresponding diaqua complex shows (−) and (+) peaks form the lower frequency side, the (+) peak for the $(+)_{589}$ carbonato complex is assignable to the A_{2g} component.

These assignments are supported by comparison of extrema of the dominant Cotton peaks with the corresponding absorption maxima. As given in Table 2, the extrema of the dominant peaks for the $[Co(CO_3)(NH_3)_2(bpy)]^+$, $[Co(O,O)(en)_2]^+$ and $[Co(O,O)(NH_3)_2(en)]^+$ complexes shift to lower frequencies compared with the corresponding absorption maxima, and the extremum for the $[Co(CO_3)(en)(py)_2]^+$ complex to a higher frequency than its absorption maximum. In the case of the $[Co(O,O)(N)_4]^+$-type complexes, the mutual cancellation of the two components, which have opposite sign and correspond to the $A_{1g}\rightarrow A_{2g}$ and $A_{1g}\rightarrow E_g$ transitions, would tend to shift the observed extremum for the former component to lower energies than the absorption maximum. On this basis, the dominant peaks of the $[Co(CO_3)(NH_3)_2(bpy)]^+$, $[Co(O,O)(en)_2]^+$, and $[Co(O,O)(NH_3)_2(en)]^+$ complexes are assignable to the A_{2g} component, and the dominant peak of the $[Co(CO_3)(en)(py)_2]^+$ complex to the E_g component.

Absolute Configuration. The (+) peak of $(+)_{546}[Co(ox)(en)_2]^+$ is assignable to the A_{2g} component and the absolute configuration has been known as Λ.[8] Since the (+) peaks of $(+)_{546}[Co(CO_3)(en)_2]^+$, $(+)_{589}[Co(CO_3)(NH_3)_2(en)]^+$, $(+)_{589}[Co(CO_3)(NH_3)_2(bpy)]^+$, $(+)_{589}[Co(ox)(NH_3)_2(en)]^+$, $(+)_{589}[Co(mal)(en)_2]^+$ and $(+)_{589}[Co(mal)(NH_3)_2(en)]^+$ are assignable to the A_{2g} component, the absolute configurations of the above six complexes are assignable to Λ. The facts that $(+)_{546}[Co(ox)(en)_2]^+$ and $(+)_{589}[Co(ox)(NH_3)_2(en)]^+$ are derived from $(+)_{546}[Co(CO_3)(en)_2]^+$ and $(+)_{589}[Co(CO_3)(NH_3)_2(en)]^+$ support the above assignments. Since the (+) peaks of $(+)_{589}[Co(CO_3)(en)(py)_2]^+$ and $(-)_{589}[Co(CO_3)(NH_3)_2(py)_2]^+$ are assignable to the E_g component, the $(+)_{589}$ complex has a Δ configuration and the $(-)_{589}$ one a S configuration, which is equivalent to a Δ configuration for the bis(chelate) complex. There is a question about the assignment of the absolute configurations of these pyridine complexes, because the dominant peak for the pyridine complexes arises from the E_g component, and that for other complexes, which contain no pyridine, from the A_{2g} component. Such a difference makes it possible that the relationship between the sign of the Cotton peak and the absolute configuration differs between a $[Co(N)_4(O)_2]$-type complex containing pyridine and that containing no pyridine ligand.

Of the $[Co(O,O)_2(N)_2]^-$-type complexes, $(-)_{546}[Co(ox)_2(en)]^-$ has been known to have a Λ configuration.[9] Since the (+) peak for this complex is assigned to the E_g component, the peak corresponding to the E_g component for this type of complex in Λ configuration may have (+) sign. The (+) peak of $(-)_{589}[Co(CO_3)(ox)(en)]^-$ is assigned to the E_g component. Therefore, the absolute configuration of this $(-)_{589}$ complex is assignable to Λ. The fact that $(-)_{546}[Co(ox)_2(en)]^-$ is derived from $(-)_{589}[Co(CO_3)(ox)(en)]^-$ supports the above assignment. In the same way, since the (+) peaks of $(+)_{589}[Co(CO_3)(ox)(tn)]^-$ and $(+)_{589}[Co(CO_3)(ox)(py)_2]^-$ are both assigned to the E_g component, the absolute configurations of these two complexes are also assignable to Λ.

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